

What is claimed is:

1. On a steel substrate a surface having a thickness from 10 to 5,000 microns comprising from 90 to 10 weight % of compounds of the formula  $Mn_xCr_{3-x}O_4$  wherein x is from 0.5 to 2 and from 10 to 90 weight % of oxides of Mn and Si selected from the group consisting of MnO, MnSiO<sub>3</sub>, Mn<sub>2</sub>SiO<sub>4</sub> and mixtures thereof provided that the surface contains less than 5 weight % of Cr<sub>2</sub>O<sub>3</sub>.
2. The surface according to claim 1, in which covers not less than 85% of the surface of the substrate.
3. The surface according to claim 2, having a thickness from 10 to 1,000 microns.
4. The surface according to claim 3, comprising from 40 to 60 weight % of said spinel and from 60 to 40 weight % oxides of Mn and Si selected from the group consisting of MnO, MnSiO<sub>3</sub>, Mn<sub>2</sub>SiO<sub>4</sub> and mixtures thereof.
5. The surface according to claim 4, wherein Cr<sub>2</sub>O<sub>3</sub> is present in an amount of less than 2 weight %.
6. A surface according to claim 5, wherein the substrate is selected from the group consisting of carbon steel, stainless steel, heat resistant

steel, HP, HT, HU, HW and HX stainless steel, and nickel or cobalt based HTA alloys.

7. The surface according to claim 6, wherein the substrate comprises from 13 to 50 weight % of Cr and from 20 to 50 weight % of Ni.

8. The surface according to claim 6, wherein the substrate comprises from 50 to 70 weight % of Ni; from 20 to 10 weight % of Cr; from 20 to 10 weight % of Co; and from 5 to 9 weight % of Fe.

9. The surface according to claim 6, wherein the substrate comprises from 40 to 65 weight % of Co; from 15 to 20 weight % of Cr; and from 20 to 13 weight % of Ni; less than 4 weight % of Fe; and up to 20 weight % of W.

10. The surface according to claim 7, wherein the oxide is MnO.

11. The surface according to claim 7, wherein the oxide is MnSiO<sub>3</sub>.

12. The surface according to claim 7, wherein the oxide is Mn<sub>2</sub>SiO<sub>4</sub>.

13. The surface according to claim 7, wherein the oxides are mixtures of MnO, MnSiO<sub>3</sub> and Mn<sub>2</sub>SiO<sub>4</sub>.

14. The surface according to claim 8, wherein the oxide is MnO.

15. The surface according to claim 8, wherein the oxide is  $\text{MnSiO}_3$ .
16. The surface according to claim 8, wherein the oxide is  $\text{Mn}_2\text{SiO}_4$ .
17. The surface according to claim 8, wherein the oxides are mixtures of  $\text{MnO}$ ,  $\text{MnSiO}_3$  and  $\text{Mn}_2\text{SiO}_4$ .
18. The surface according to claim 9, wherein the oxide is  $\text{MnO}$ .
19. The surface according to claim 9, wherein the oxide is  $\text{MnSiO}_3$ .
20. The surface according to claim 9, wherein the oxide is  $\text{Mn}_2\text{SiO}_4$ .
21. The surface according to claim 9, wherein the oxides are mixtures of  $\text{MnO}$ ,  $\text{MnSiO}_3$  and  $\text{Mn}_2\text{SiO}_4$ .
22. A method of applying a composition comprising from 90 to 10 weight % of compounds of the formula  $\text{Mn}_x\text{Cr}_{3-x}\text{O}_4$  wherein x is from 0.5 to 2 and from 10 to 90 weight % of oxides of Mn and Si selected from the group consisting of  $\text{MnO}$ ,  $\text{MnSiO}_3$  and  $\text{Mn}_2\text{SiO}_4$  and mixtures thereof provided that the composition contains less than 5 weight % of  $\text{Cr}_2\text{O}_3$  to at least a portion of a steel substrate comprising applying said composition by a method selected from the group consisting of detonation gun spraying, cement packing, hard facing, laser cladding, plasma spraying, physical vapor deposition methods, flame spraying, and electron beam

evaporation to at least 70% of the selected surface of the steel substrate to provide a thickness from 0.1 to 5,000 microns.

23. The process according to claim 22, in which the composition covers not less than 85% of the selected surface of the substrate.

24. The process according to claim 23, wherein the surface has a thickness from 10 to 1,000 microns.

25. The process according to claim 24, comprising from 40 to 60 weight % of said spinel and from 60 to 40 weight % oxides of Mn and Si selected from the group consisting of MnO, MnSiO<sub>3</sub> and Mn<sub>2</sub>SiO<sub>4</sub> and mixtures thereof.

26. The process according to claim 25, wherein Cr<sub>2</sub>O<sub>3</sub> is present in an amount of less than 2 weight %.

27. The process according to claim 26, wherein the substrate is selected from the group consisting of carbon steel, stainless steel, heat resistant steel, HP, HT, HU, HW and HX stainless steel, and nickel or cobalt based HTA alloys.

28. The process according to claim 27, wherein the substrate comprises from 13 to 50 weight % of Cr and from 20 to 50 weight % of Ni.

29. The process according to claim 27, wherein the substrate comprises from 50 to 70 weight % of Ni; from 20 to 10 weight % of Cr; from 20 to 10 weight % of Co; and from 5 to 9 weight % of Fe.
30. The process according to claim 27, wherein the substrate comprises from 40 to 65 weight % of Co; from 15 to 20 weight % of Cr; and from 20 to 13 weight % of Ni, less than 4 weight % of Fe and up to 20 weight % of W.
31. The process according to claim 28, wherein the oxide is MnO.
32. The process according to claim 28, wherein the oxide is MnSiO<sub>3</sub>.
33. The process according to claim 28, wherein the oxide is Mn<sub>2</sub>SiO<sub>4</sub>.
34. The process according to claim 28, wherein the oxides are mixtures of MnO, MnSiO<sub>3</sub> and Mn<sub>2</sub>SiO<sub>4</sub>.
35. The process according to claim 29, wherein the oxide is MnO.
36. The process according to claim 29, wherein the oxide is MnSiO<sub>3</sub>.
37. The process according to claim 29, wherein the oxide is Mn<sub>2</sub>SiO<sub>4</sub>.

38. The process according to claim 29, wherein the oxides are mixtures of MnO, MnSiO<sub>3</sub> and Mn<sub>2</sub>SiO<sub>4</sub>.
39. The process according to claim 30, wherein the oxide is MnO.
40. The process according to claim 30, wherein the oxide is MnSiO<sub>3</sub>.
41. The process according to claim 30, wherein the oxide is Mn<sub>2</sub>SiO<sub>4</sub>.
42. The process according to claim 30, wherein the oxides are mixtures of MnO, MnSiO<sub>3</sub> and Mn<sub>2</sub>SiO<sub>4</sub>.
43. A stainless steel pipe or tube having at least a portion of its inner surface comprising a composite surface according to claim 1.
44. A stainless steel reactor having at least a portion of its inner surface comprising a composite surface according to claim 1.
45. A stainless steel heat exchange having at least a portion of its inner surface comprising a composite surface according to claim 1.
46. A process for the thermal cracking of a hydrocarbon comprising passing said hydrocarbon at elevated temperatures through stainless steel tubes, pipes, or coils according to claim 43.

47. A process for altering the enthalpy of a fluid comprising passing the fluid through a heat exchanger according to claim 45.

48. A process for conducting a chemical reaction in a stainless steel reactor according to claim 44.